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14. ABSTRACT Polycyanurate thermosetting networks, polycarbonate thermoplastics, and homogenous polycarbonate/polycyanurate network blends have been prepared from a bio-derived bisphenol. The bisphenol was prepared via a solvent-free, ruthenium-catalyzed olefin metathesis coupling reaction of eugenol followed by hydrogenation. The pure polycyanurate network exhibited a glass transition temperature (T <sub>g</sub> ) of 186 degrees Celsius and a 5% weight loss temperature above 350 degrees Celsius under nitrogen. The pure polycarbonate exhibited a T <sub>g</sub> of 71 degrees Celsius, M <sub>n</sub> = 8360, and a polydispersity of 1.88. No phase separation was observed in an 80:20 blend of cyanate ester: polycarbonate during or after cure; the resulting homogeneous system showed a single T <sub>g</sub> of 132 degrees Celsius. End-group analysis of the polycarbonate provided no evidence of residual phenols, and the polycarbonate fraction was readily extracted from the polycyanurate network, suggesting that no chemical grafting occurred. These new polymer systems represent promising potential alternatives to similar systems derived from Bisphenol A.					
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# **POLYCYANURATES AND POLYCARBONATES BASED ON EUGENOL: ALTERNATIVES TO THERMOSETTING AND THERMOPLASTIC POLYMERS BASED ON BISPHENOL A**

14 August 2014

**Andrew J. Guenthner<sup>1</sup>, Benjamin G. Harvey<sup>2</sup>, Gregory R. Yandek<sup>1</sup>, Lee R. Cambrea<sup>2</sup>, Heather A. Meylemans<sup>2</sup>, Lawrence C. Baldwin<sup>2</sup>, Josiah T. Reams<sup>3</sup>, Christopher M. Sahagun<sup>4</sup>, Joseph M. Mabry<sup>1</sup>**

**<sup>1</sup>Aerospace Systems Directorate, Air Force Research Laboratory**

**<sup>2</sup>Naval Air Warfare Center, Weapons Division**

**<sup>3</sup>ERC Incorporated**

**<sup>4</sup>National Research Council / Air Force Research Laboratory**

**Ph: 661/275-5769; e-mail: [andrew.guenthner@us.af.mil](mailto:andrew.guenthner@us.af.mil)**

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# Outline



- Eugenol Polycyanurates:
  - Low Moisture Uptake
- Eugenol Polycarbonates
  - Flexible Backbone
- Eugenol Polycyanurate Toughened with Eugenol Polycarbonate
  - High Compatibility



Acknowledgements: Strategic Environmental Research and Development Program (SERDP); Air Force Office of Scientific Research (AFOSR)  
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# AFRL Mission



*Leading the discovery, development, and integration of affordable warfighting technologies for our air, space, and cyberspace force.*





# Cyanate Esters for Next-Generation Aerospace Systems



Glass Transition Temperature  
200 – 400 °C (dry)  
150 – 300 °C (wet)

Resin Viscosity  
Suitable for  
Filament  
Winding / RTM

Compatible with  
Thermoplastic  
Tougheners and  
Nanoscale  
Reinforcements

High  $T_g$

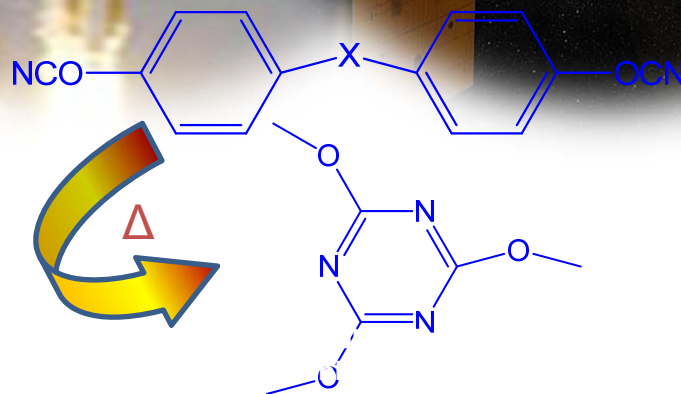
Onset of Weight Loss:  
> 400 °C with High  
Char Yield

Ease of  
Processing

Resistance to  
Harsh  
Environments

Good Flame,  
Smoke, &  
Toxicity  
Characteristics

Low Water Uptake  
with Near Zero  
Coefficient of  
Hygroscopic  
Expansion



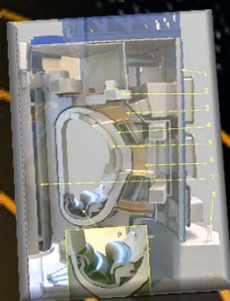


# Cyanate Esters Around the Solar System



## Our Solar System

- On Earth, cyanate ester / epoxy blends have been qualified for use in the toroidal field magnet casings for the ITER thermonuclear fusion reactor



Fusion reactor, photo courtesy of Gerritse ((Wikimedia Commons))

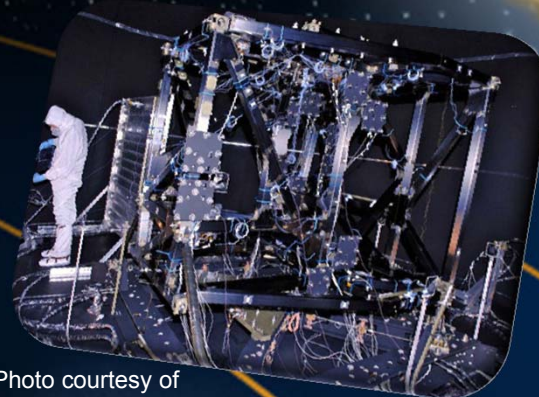


Photo courtesy of NASA

- Unique cyanate ester composites have been designed by NASA for use as instrument holding structures aboard the James Webb Space Telescope
- The science decks on the Mars Phoenix lander are made from M55J/cyanate ester composites
- The solar panel supports on the MESSENGER space probe use cyanate ester composite tie layers

Images: courtesy NASA (public release)



# Why Bio-Based Cyanate Esters



- Materials qualification efforts are costly; developing bio-based materials that deliver both improved performance and decreased dependence on petroleum enables a higher and more robust return on investment
- Cyanate esters are generally easy to process; they do not require stoichiometric balance and form co-networks readily, hence they tolerate variation in monomer chemistry relatively well
- The superior flame, smoke, and toxicity characteristics of cyanate esters, the excellent adhesion and durability characteristics of the networks, and the very high selectivity of the reaction (which makes de-polymerization easier), all confer benefits from a sustainability perspective
- Bio-based feedstocks for cyanate esters are interesting because of the combinations of physical properties provided by structure of the molecules themselves, not just because of the cost or environmental impacts
- Bio-based materials offer potential alternatives to the use of Bisphenol A



U.S. Navy photo by Photographer's Mate  
3rd Class Mark J. Rebilas (RELEASED)





# Toughening Polycyanurates

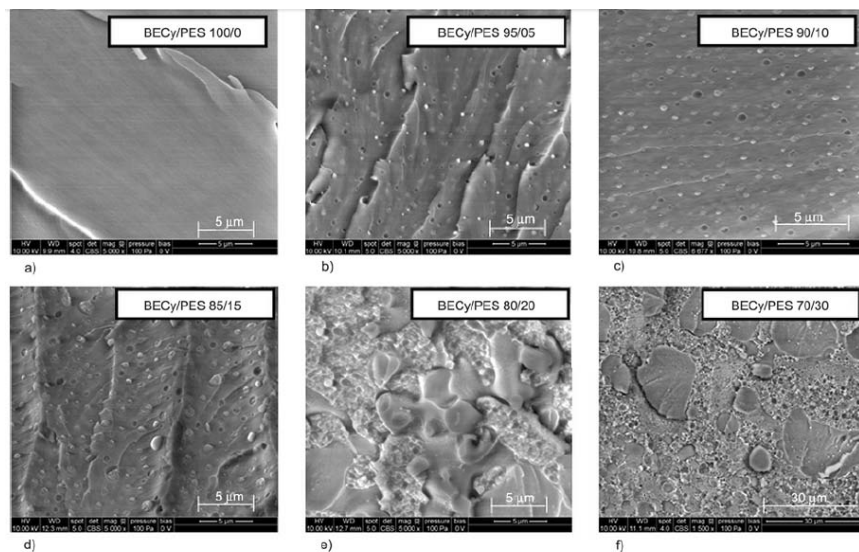


Figure 3. SEM micrographs of BECy/PES blends containing: a) 0, b) 5, c) 10, d) 15, e) 20, and f) 30 wt% PES

*Thunga et al. – eXPRESS Polymer Letters  
Vol.8, No.5 (2014) 336–344.*

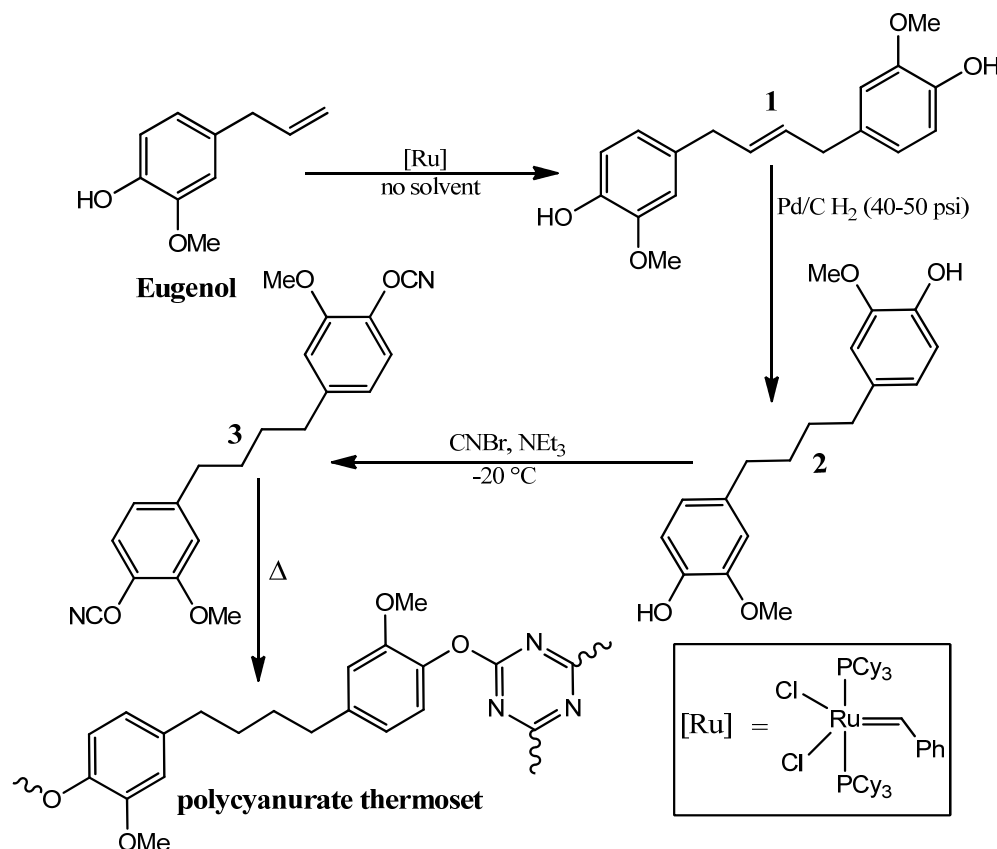
Recent work from the Kessler group illustrating the effect of loading level on morphology of polycyanurate toughened with poly(ether sulfone).

- Rubber particles can be used (as with epoxies) but with a thermal performance penalty.
- Thermoplastics may be added and will form a separate micro-phase during cure; the thermoplastic domains act like rubber particles, but with improved thermal stability. The phase separation process must be carefully controlled.
- Nanoparticles such as silica can be added, but these may introduce difficulties in composite processing.
- Compatible thermoplastics that do not undergo phase separation offer thermal stability and easy processing, but may not improve toughness as much as other methods.





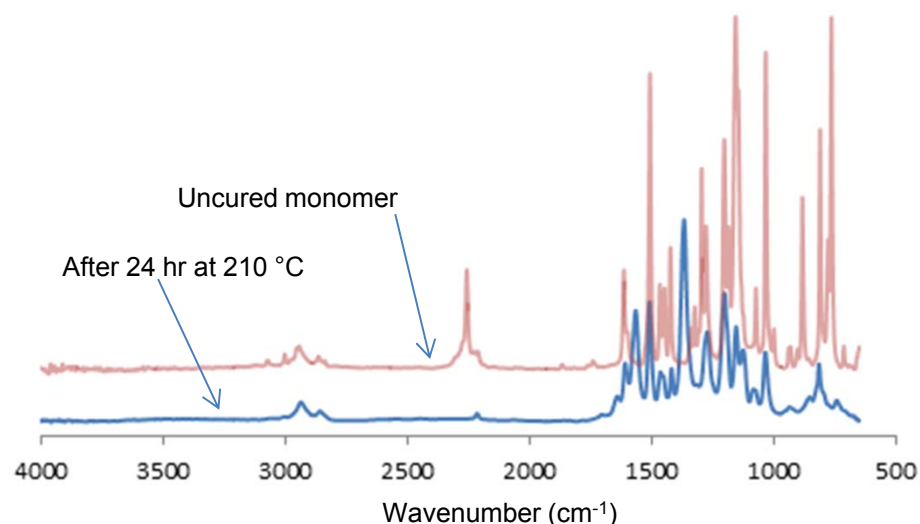
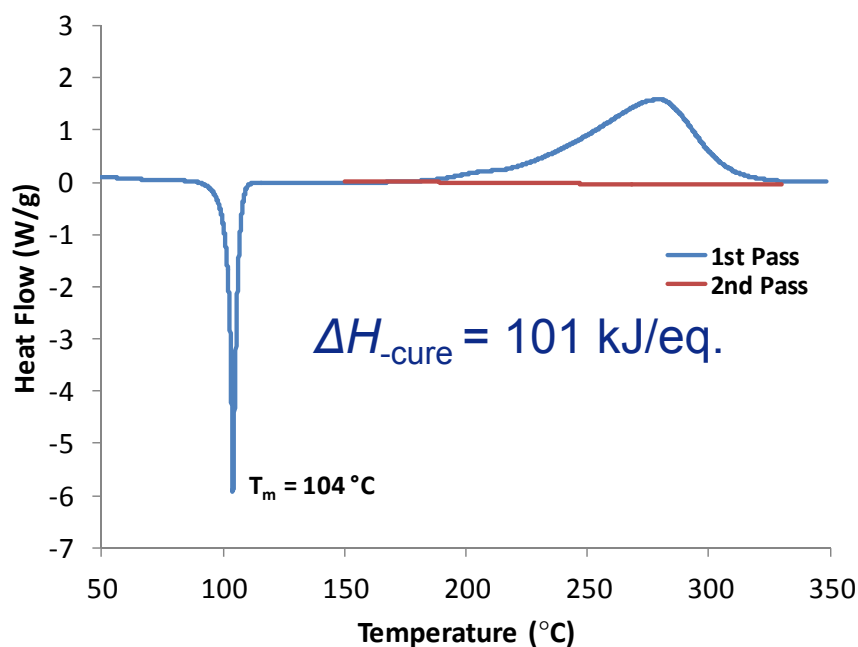
# Synthesis of Eugenol CE



- The terminal vinyl group on eugenol serves as a handle for Ru-catalyzed coupling. The coupled product may be reduced to eliminate the double bond for increased molecular flexibility. The resulting polyphenol is then readily converted to the di(cyanate ester) using cyanogen halide treatment, and thermally cyclotrimerized.



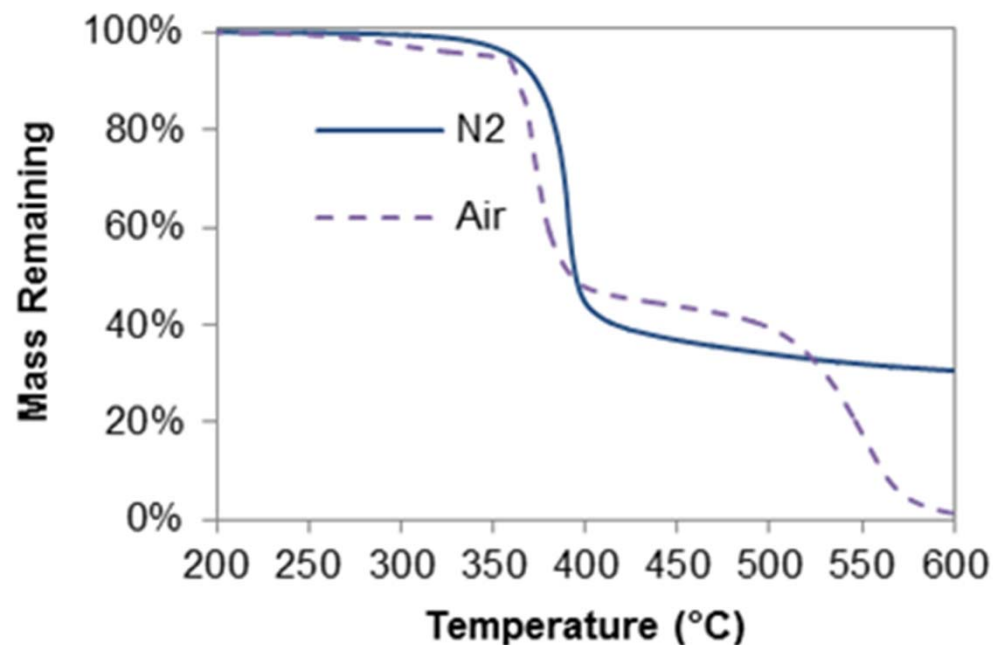
# DSC and FT-IR of Eugenol CE



- Melting point is in line with expectations for a larger, symmetric cyanate ester monomer. Heat of reaction and exotherm temperature indicate reasonable purity for synthesis at the 1-gram scale.
- FT-IR confirms cure proceeds normally, with near complete conversion to cyanurate at modest temperatures.



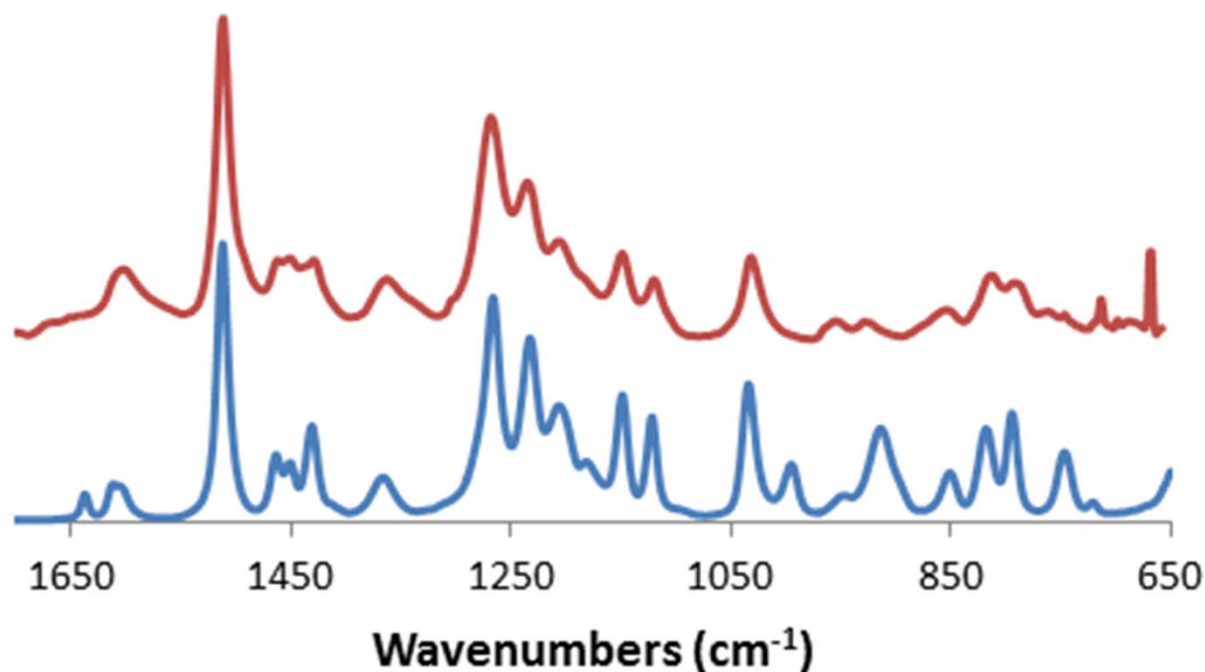
# TGA of Eugenol CE



- The methoxy groups as well as the large aliphatic bridge reduce char yield compared to many cyanate esters, but a high onset of decomposition is still maintained.
- Other key properties of the cured eugenol CE include a  $T_g$  near 190 °C and a moisture uptake of 1.8% after 96 hours of immersion in water at 85 °C.



# Thermal Degradation of Eugenol CE Yields Eugenol!

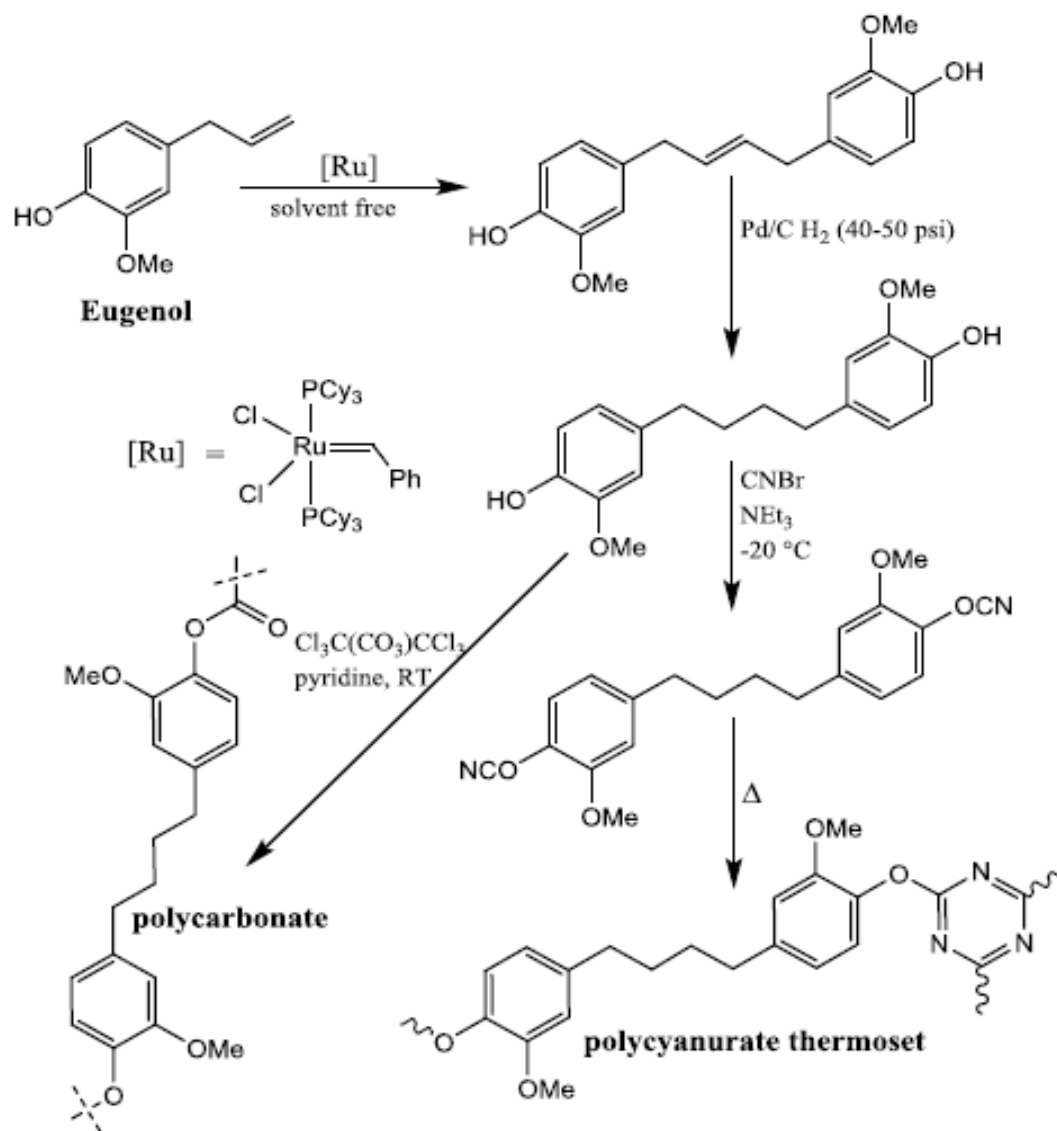


- FT-IR of eugenol (blue) is closely related to FT-IR collected by TGA/IR of eugenol CE decomposition at 400 °C.
- As a product of decomposition, eugenol is an environmentally-friendly alternative to Bisphenol A.





# Synthesis of Thermoplastic and Thermoset Polymers from Eugenol

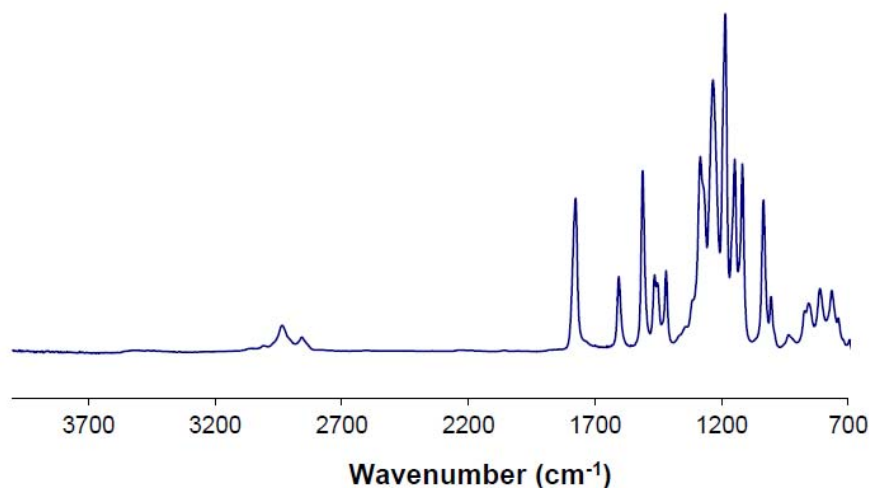




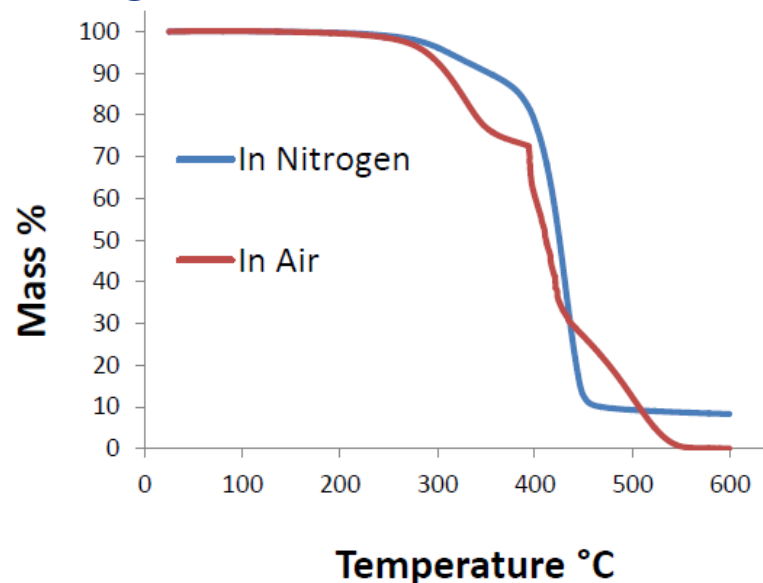
# Eugenol Polycarbonate Properties



FT-IR



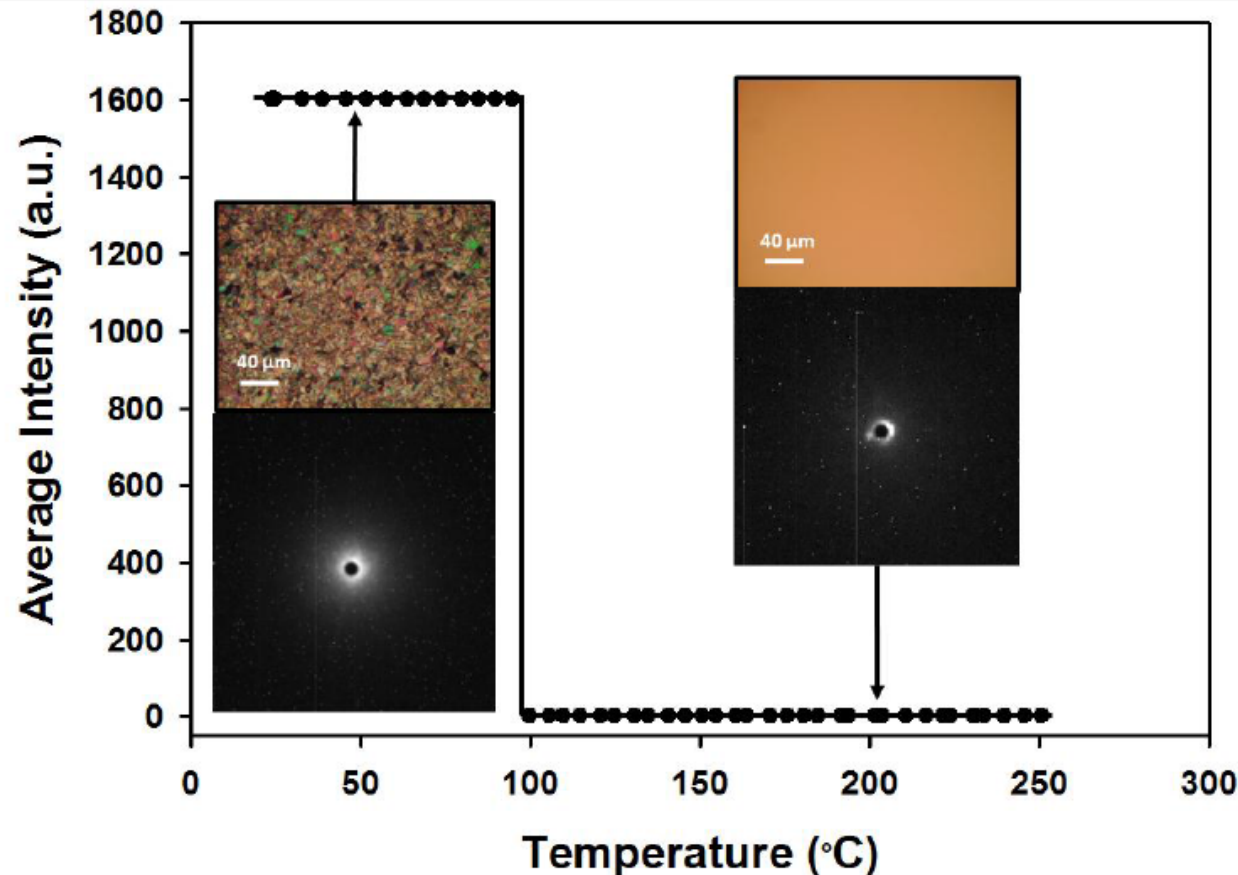
TGA



- DSC indicates  $T_G$  values between 50 and 70 °C.
- $M_n$  for batch 1, 4300 g/mol (PDI 2.25);  $M_n$  for batch 2, 8400 g/mol (PDI 1.88)
- No evidence yet seen of phenol end groups by <sup>1</sup>H NMR or FT-IR.



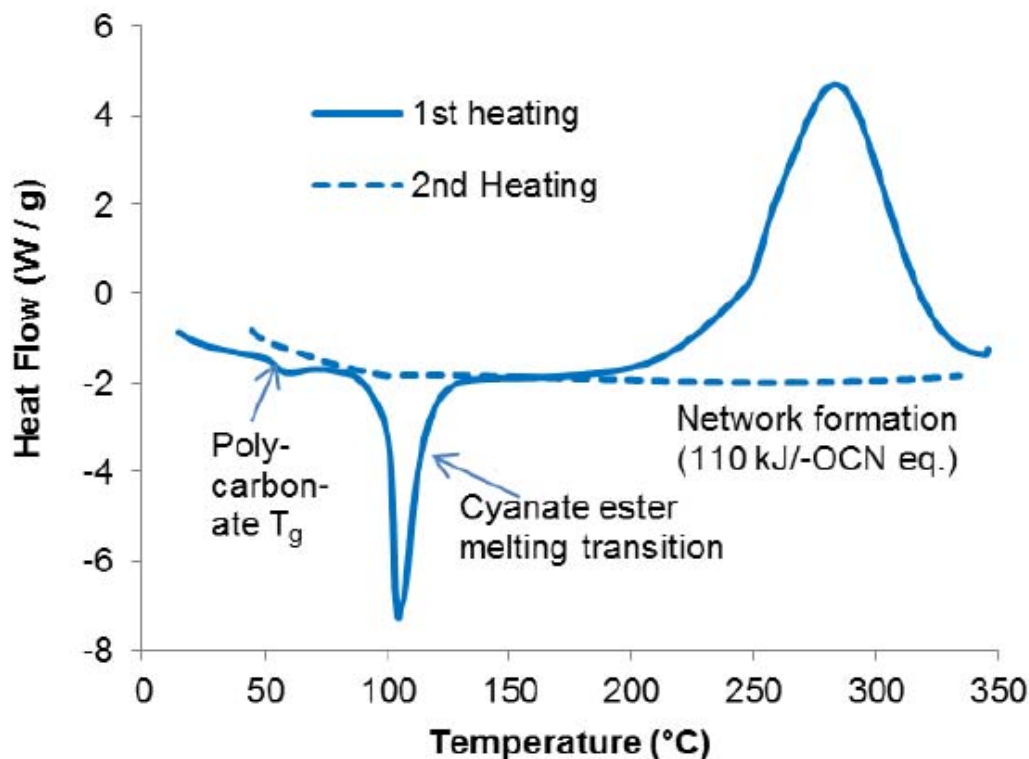
# SALLS of Eugenol PC / CE Blend



- Heating ramp experiment from solid monomer to cured resin.
- 20 wt% polycarbonate in CE monomer shows depression of melting point, but no phase separation during subsequent cure.



# DSC of Eugenol Polycarbonate / Eugenol CE Blend



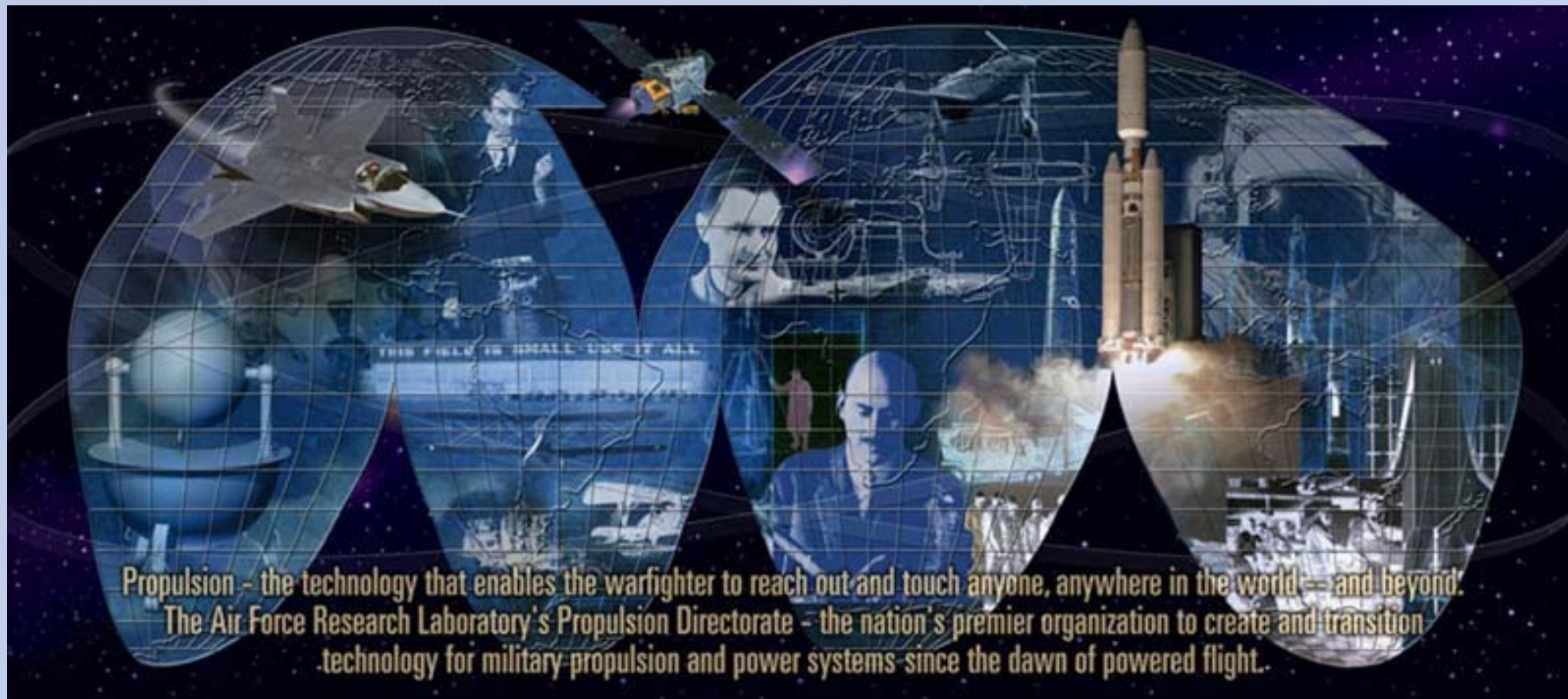
- DSC confirms that cure has taken place over temperatures where no light scattering pattern emerges. Cured samples are transparent and homogeneous with a TG of around 125 °C.





# Summary

- The naturally occurring substance eugenol was successfully converted to both a thermosetting monomer (cyanate ester) and a thermoplastic polycarbonate.
- The decomposition of the cured cyanate ester yielded a significant quantity of eugenol, demonstrating both an interesting possibility for regeneration of monomer at the end of service as well as an alternative to generation of Bisphenol A.
- The physical properties of both the cured cyanate ester network as well as the polycarbonate were in line with expectations based on the chemical structure.
- The high level of chemical similarity between the cyanate ester and the polycarbonate appears to have led to very high compatibility, making possible the formation of a toughened thermosetting resin by homogeneous incorporation of thermoplastic.



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